Alkoxy Nitroxide Radicals from Photolysis of Nitropyridines: a Kinetic Investigation by Electron Spin Resonance Spectroscopy [1]

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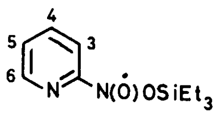
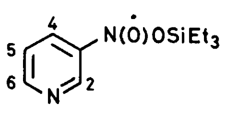
Triethylsilyloxy nitroxide radicals obtained by photolysis from the three isomeric nitropyridines have been investigated by e.s.r. spectroscopy. The kinetic study showed a first-order decay of the radicals; the concentration was found to depend upon the square root of the light intensity and therefore a reaction mechanism is postulated involving the reversible formation of a diamagnetic dimer. Proof of this was obtained by rapidly raising the temperature during the course of radical decay.

THE photolysis of aromatic nitro-derivatives in the presence of hydrogen donating solvents has been shown to yield radicals,[2] detectable by e.s.r. techniques,[3–7] with the general formula $ArN\dot{O}{-}OR$.[3–5] Information on the spin density distribution, conformational properties, and stereodynamic behaviour have been obtained. However, the kinetics of the decay processes of these radicals have not been investigated to the same degree. In the present work particular attention has been paid to this aspect by studying the photolytic processes of the three isomeric nitropyridines whose alkoxy nitroxides had not previously been observed.



(1)



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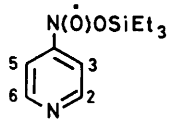

(3)

TABLE 1

Hyperfine splitting constants (G) of radicals (1)—(4)

Radical	a_{H1}	a_{H2}	a_{H3}	a_{H4}	a_{H5}	a_{H6}	a_N	a_{NO}
(1)			2.95	0.80	2.85	0.80	1.45	13.45
(2)		3.20		3.40	1.08	3.00	1.08	14.20
(3)		0.70	3.00		3.00	0.70	1.80	12.85
(4)	3.10	1.04	3.10		3.10	1.04		14.76

For the sake of comparison the pyridine nitroxides ($C_5H_4N{-}N\dot{O}H$) have also been examined.

RESULTS AND DISCUSSION

(a) *E.s.r. Spectra and Configurational Properties.*—The radicals (1)—(3) have been obtained by photolysing Et_3SiH solutions of 2-, 3-, and 4-nitropyridines inside the cavity of the e.s.r. spectrometer. The mechanism of the reaction of the nitro-derivatives to give the triethylsilyloxy nitroxides (1)—(3) has already been discussed.[3,6,7]

A typical e.s.r. spectrum is given in Figure 1 and the parameters used for the computer simulation are reported in Table 1. It can be observed that the a_{NO} hyperfine splittings in the three isomeric derivatives parallel the trend of the corresponding nitropyridine radical anions [8] (Figure 2a); this also holds with respect to the a_N splitting of the heterocyclic nitrogen (Figure 2b). It has been recognized [6,9] that the hyperfine splitting constants of a group bonded to an aromatic ring ($N\dot{O}{-}OSiEt_3$ in the present case) are affected by the electron-delocalizing ability of the ring itself: the smaller the splitting, the larger is the delocalization of the unpaired electron on the aromatic substituent. Accordingly the trend observed for a_{NO} in Table 1 indicates that the delocalization sequence is 4-pyridyl > 2-pyridyl > 3-pyridyl > phenyl.

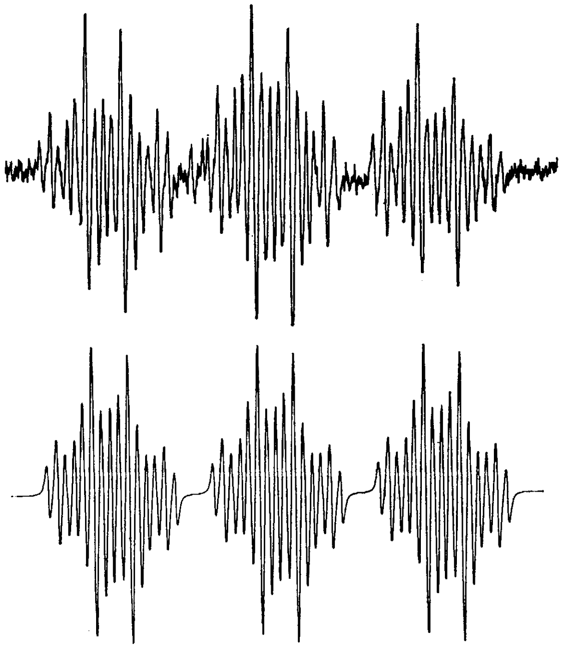

FIGURE 1 Experimental (upper) and simulated e.s.r. spectrum of radical (1) at −20 °C

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[1] Taken in part from N. Ronchi, Doctoral Thesis, University of Bologna.

[2] I. A. Barltrop and N. J. Brunce, *J. Chem. Soc. (C)*, 1968, 1467.

[3] D. J. Cowley and L. H. Sutcliffe, *J. Chem. Soc. (B)*, 1970, 569.

[4] R. B. Sleight and L. H. Sutcliffe, *Trans. Faraday Soc.*, 1971, **67**, 2195.

[5] S. K. Wong and J. K. S. Wan, *Canad. J. Chem.*, 1973, **51**, 753.

[6] C. M. Camaggi, L. Lunazzi, and G. Placucci, *J. Org. Chem.*, 1974, **39**, 2425.

[7] C. M. Camaggi, L. Lunazzi, G. F. Pedulli, G. Placucci, and M. Tiecco, *J.C.S. Perkin II*, 1974, 1226.

[8] A. Gamba, V. Malatesta, G. Morosi, C. Oliva, and M. Simonetta, *J. Phys. Chem.*, 1973, **77**, 2744.

[9] L. Lunazzi, A. Mangini, G. F. Pedulli, and M. Tiecco, *Gazzetta*, 1971, **101**, 10.

For a similar reason the a_N splitting of the heterocyclic nitrogen in (1)—(3) should follow the opposite trend for, the larger the delocalizing power of the ring, the larger is also expected to be the spin density (and thus a_N) on the pyridyl nitrogen. Actually the a_N value in (3) (1.8 G) is larger than in (1) (1.45 G) and (2) (1.08 G).

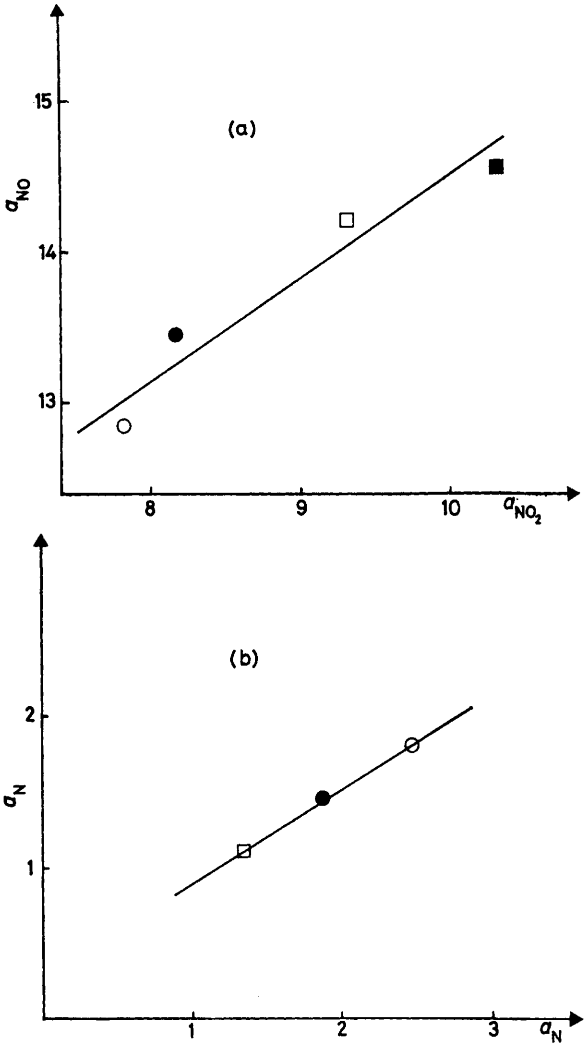
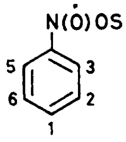


FIGURE 2 (a) Plot of hyperfine splitting constants a_{NO} (G) of triethylsilyloxy nitroxide radicals (1) (●), (2) (□), (3) (○), and (4) (■) against hyperfine splitting constants a_{NO_2} (G) of the corresponding nitropyridine radical anions. (b) Plot of hyperfine splitting constants a_N (G) of the heterocyclic nitrogen in trimethylsilyloxy nitroxide radicals (1) (●), (2) (□), and (3) (○) against hyperfine splitting constants a_N (G) of the heterocyclic nitrogen in the corresponding nitropyridine radical anions (abscissa)

A further point worth discussing concerns the conformation of these nitroxides, for one should expect restricted rotation about the $Ar{-}N(\dot{O})OR$ bond as in the case of furyl,[6] thienyl,[7] and thiazolyl [10] alkoxy nitroxides where the two possible rotational conformers were identified. Effects due to such restricted rotation, however, were not observed in (1)—(3) thus leaving essentially two possible explanations. (i) The differences in the hyperfine splitting constants [and for (1) and (2) in the g factor] are too small for detecting two different e.s.r. spectra. (ii) The rotational barrier is lower than that of the mentioned five-membered heterocyclic alkoxy nitroxides.[6,7,10]

The first hypothesis certainly applies to phenyl triethylsilyloxy nitroxide (4) which does not show, at low temperatures, non-equivalence of the o-hydrogen atoms, whereas phenyl nitroxide (5) does.[7,11]



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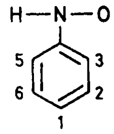
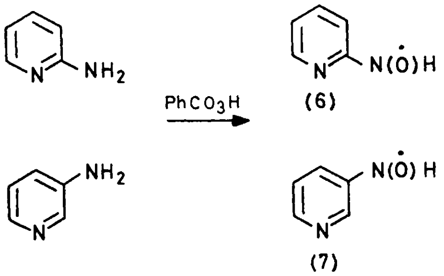


(5)

To see whether behaviour analogous to that of (5) could be observed in the corresponding pyridine-containing radicals, we obtained the nitroxide radicals (6) and (7) by oxidizing with perbenzoic acid 2- and 3-aminopyridine in 1,2-dimethoxyethane as solvent. The hyperfine splitting constants are collected in Table 2. Despite many attempts oxidation of 4-aminopyridine under the same conditions did not afford the corresponding nitroxide radical in sufficient amount and stability to identify its e.s.r. spectrum.

Although the oxidation of aminopyridines could yield in principle the corresponding N-oxide derivatives of radicals (6) and (7), we could eliminate this possibility. The a_N values of heterocyclic nitrogen are much larger in radicals containing the N-oxide group than in analogous radicals containing the non-oxidized pyridine ring. For instance in the radical anions of pyridine and quinoline N-oxides a_N is 10.9 and 6.0 G respectively [12,13] and is 6.3 and 3.8 G in pyridine and quinoline.[12,13]



SCHEME 1

The small a_N values observed for (6) and (7) (1.45 and 1.00 G respectively) are very close to those of (1) and (3) (1.45 and 1.08 G respectively); since the latter radicals cannot have the heterocyclic nitrogen oxidized because of the method of generation, (6) and (7) should not be N-oxide radicals. The spectra of (6) and (7), even at the lowest attainable temperature ($ca.$ −60°) do not show,

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[10] A. Alberti, M. Guerra, G. F. Pedulli, and M. Tiecco, *Gazzetta*, 1974, **104**, 1301.

[11] Th. A. J. W. Wajer, A. Mackor, Th. J. de Boer, and J. D. W. Van Voorst, *Tetrahedron Letters*, 1967, 1941.

[12] C. T. Talcott and R. J. Myers, *Mol. Phys.*, 1967, **12**, 549; L. Lunazzi, A. Mangini, G. F. Pedulli, and F. Taddei, *J. Chem. Soc.* (*B*), 1970, 163.

[13] T. Kubota, K. Nishikida, H. Miyazaki, K. Iwatani, and Y. Oishi, *J. Amer. Chem. Soc.*, 1968, **90**, 5080; L. Lunazzi, A. Mangini, G. Placucci, and F. Taddei, *J. Chem. Soc.* (*B*), 1970, 440.

as opposed to phenyl nitroxide (5), evidence of restricted rotation. Accordingly there is an inclination to conclude that the rotational barrier in these radicals is smaller than that of the corresponding phenyl,[7] as well as of some five-membered heterocyclic compounds.[6,7,10] This conclusion, however, seems to contradict the fact that in similar molecules (*i.e.* pyridine-2- and -3-carbaldehydes) the rotational barriers (7.3 and 7.6 kcal mol^{-1} respectively [14]) are quite close to those of benzaldehyde itself [15] (7.70 kcal mol^{-1}).

An alternative possibility that explains the failure in detecting the two conformers is that in nitroxides (6) and (7) only one of the two possible rotamers is present in sufficient amount for detection. This is in better agreement with the findings for pyridinecarbaldehydes where the *ON-trans*-rotamer was found in much larger amount than the *ON-cis* (80% in pyridine-2- and 93% in -3-carbaldehyde). Therefore the spectra of (6) and (7) might not result from the superimposition of two spectra, since only the *trans*-conformer (if the analogy between NHO and CHO is valid) would be present in detectable amount.

TABLE 2

Hyperfine splitting constants (G) of radicals (5)—(7)

Radical	a_{H1}	a_{H2}	a_{H3}	a_{H4}	a_{H5}	a_{H6}	a_{H}(NO)	a_{N}	a_{NO}
(5)	3.07	1.00	3.07		2.74	1.00	12.12		9.13
(6)			2.85	0.82	2.85	0.82	12.13	1.45	8.07
(6a) *			(−1.40)	(0.79)	(−1.24)	(0.83)	(−8.50)	(1.00)	(4.72)
(6b) *			(−1.44)	(0.78)	(−1.27)	(0.88)	(−8.46)	(0.87)	(4.82)
(7)		2.60		3.15	1.00	3.00	12.45	1.00	8.40
(7a) *		(−1.41)		(−1.55)	(0.87)	(−1.24)	(−9.18)	(−0.71)	(5.16)
(7b) *		(−1.43)		(−1.49)	(0.79)	(−1.22)	(−9.15)	(−0.71)	(5.14)

* The values in parentheses are the theoretical coupling constants computed by INDO calculations for the conformer *cis* (a) or *trans* (b) to the heterocyclic nitrogen atom.

For this purpose, theoretical INDO calculations were also performed for (6) and (7). Although they are not in complete agreement with experiment, particularly for the a_N and a_H splittings of the NOH group, they predict, in both (6) and (7), a lower energy for the *trans*- (−77.911 5 a.u.) than for the *cis*-rotamer (−77.909 6 a.u.). Even if the energy values obtained are considered only qualitatively (the energy differences are not too large), they lead us to suppose that the *trans*-conformers are considerably more stable and thus present in larger amounts than the *cis*-conformers, as observed for the pyridinecarbaldehydes. It can be seen that in both (6) and (7) the differences of the hyperfine splitting constants and the computed splittings are not very large for the two possible conformers.

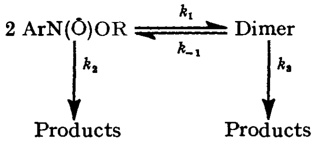
These computations were thus employed for assigning trends of the a_H values into the ring positions. The assignments for (1)—(3) were also performed by analogy with that computed for the nitroxides.

(b) *Kinetic Measurements*.—The decay of several alkoxy aryl nitroxides generated by photolysis of nitroaromatic compounds in ethers has been shown to occur with first-order kinetics.[3,4] For the radical derived from 2,3,5,6-tetrachloronitrobenzene in tetrahydrofuran unimolecular scission of the N–OR bond was proposed.[3,4]

$$\mathrm{ArN(\dot{O})OR} \longrightarrow \mathrm{ArN{=}O} + \mathrm{RO}\cdot$$

However, the Arrhenius parameters for the decay of other nitroxides [4] show too wide variations for their decompositions to occur by such a simple process. One of the final products in such reactions is the appropriate aniline.[2]

It has been shown several times [16,17] that first-order radical decay kinetics do not automatically imply a unimolecular process. These kinetics can arise because the radical is in equilibrium with a diamagnetic dimer, if the latter is present in greater concentration than the radical.[16,17] According to Scheme 2, the measured



SCHEME 2

first-order rate constant for decay, k^1_{epr}, is given either by $k_3/2$, or by $k_2k_{-1}/2k_1$, depending on whether the final products are formed directly from two radicals or from the radicals by way of the dimer.[16,17]

In the present work, the concentrations of radicals (1)—(3) are found to depend on the square root of the light intensity. This suggests, but does not require,[17c] decay by one of the processes of Scheme 2.

Further support for the existence of dimers in equilibrium with these three radicals came from temperature jump experiments. The radical was generated at −20 °C; upon cessation of photolysis, decay of the radical is relatively slow and during the course of the decay the temperature was rapidly raised to 0 °C. The radical concentration increased initially and then decreased rapidly (Figure 3). The increase in the radical concentration upon raising the temperature implies that the radical is in equilibrium with a dimer. These radicals must, therefore, all decay according to one (or both) of the routes outlined in Scheme 2. Some other

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[14] T. Drakenberg, *J.C.S. Perkin II*, 1976, 147; L. Lunazzi, D. Macciantelli, and G. Cerioni, *ibid.*, 1791.

[15] L. Lunazzi, D. Macciantelli, and A. Boicelli, *Tetrahedron Letters*, 1975, 1205; T. Drakenberg, R. Jost, and J. M. Sommer, *J.C.S. Chem. Comm.*, 1974, 1011.

[16] S. A. Weiner and L. R. Mahoney, *J. Amer. Chem. Soc.*, 1972, **94**, 5029.

[17] (*a*) J. L. Brokenshire, J. R. Roberts, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 7040; (*b*) V. Malatesta and K. U. Ingold, *ibid.*, 1974, **96**, 3949; (*c*) R. A. Kaba, L. Lunazzi, D. Lindsay, and K. U. Ingold, *ibid.*, 1975, **97**, 6762; (*d*) R. A. Kaba and K. U. Ingold, *ibid.*, in the press.

ArN(Ȯ)OR radicals that have been investigated,[2-4] particularly those which decay with first-order kinetics,[3,4] may follow similar routes.

The overall rate constants for decay of radicals (1)—(4) (*i.e.* k^1_{epr}) were determined over a temperature range from −33 to 25 °C. The derived activation energies, E^1_{epr}, and Arrhenius factors, A^1_{epr}, are listed in Table 3.

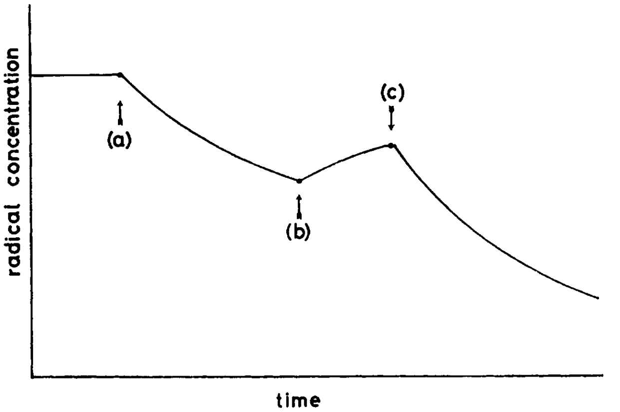

FIGURE 3 Effect of raising the temperature during the decay of triethylsilyloxy nitroxide radical from nitrobenzene: (a) end of photolysis, −20°; (b) temperature raised; (c) 0°

The *A* factors are unusually low for a first-order process [*i.e.*, $\Delta S^\ddagger$ is large and negative, as has been noted previously for the decay of other ArN(Ȯ)OR radicals [4]]. This would imply that decay *via* reaction k_2 of Scheme 2 is rather unlikely. If decay occurs *via* reaction k_3 of Scheme 2 the dimer must decompose irreversibly by way of a highly ordered transition state. For example, if head-to-tail coupling of the nitroxides occurs, as would be anticipated,[18] decomposition might involve a four-membered cyclic transition state.

TABLE 3

Rate constants at 0 °C and Arrhenius parameters for decay of radicals (1)—(4) in triethylsilane

Radical	$10^3k^1_{epr}/s^{-1}$ at 0 °C	E^1_{epr}/kcal mol^{-1}	log A^1_{epr}
(1)	5.5	$3.80_5 \pm 0.11$	0.79 ± 0.09
(2)	6.8	7.50 ± 0.30	3.83 ± 0.25
(3)	4.1	$3.70_5 \pm 0.16$	0.58 ± 0.13
(4)	8.7	10.52 ± 1.31	6.37 ± 1.10

However, it does not seem reasonable that the *A* factors for decay of (1)—(4) should differ so greatly if the decays occur by a cyclic process of the above (or analogous) type in all four cases.

This view is further emphasized by the fact that at any one temperature the actual measured values of k^1_{epr} are similar for all four radicals (see Table 3). There is therefore, a distinct possibility that the variation in the Arrhenius parameters of Table 3 reflects experimental uncertainties in the measurement of k^1_{epr} at the highest and lowest temperatures rather than reflecting a unique decay process for each radical. For radicals that decay rather slowly, the kinetic e.s.r. spectroscopic technique suffers from a number of problems of which the most important are diffusional processes and trace catalysis or inhibition. Thus, the radicals are generated photochemically in the most sensitive region of the spectrometer cavity. They may then diffuse to less sensitive regions (giving the appearance of decay) or to the walls (where they may actually decay by reaction with absorbed species [19]). The decay behaviour of 3,5-di-t-butylphenoxyl radicals, for example, in the presence of acid provides an excellent example of catalytic decay.[20] By analogy, the decomposition of the nitroxide dimer was expected to be acid catalysed and, indeed, the addition of toluene-*p*-sulphonic acid [20] did increase the measured rates of nitroxide decay.

In conclusion, we believe we have shown that the alkoxy aryl nitroxides studied in this work are in equilibrium with a dimer and that this dimer lies on the reaction pathway for radical decay. However, the detailed mechanism by which the dimers decompose, as well as the overall mechanism for the decay of the radicals, cannot possibly be unravelled until detailed product analyses are undertaken. Further work is in progress.

EXPERIMENTAL

Materials.—2-, 3-, and 4-Nitropyridines were obtained as described in the literature.[21] Nitrobenzene was purified by distillation, whereas the other starting compounds were obtained commercially and used without further purification.

E.s.r. Measurements.—E.s.r. spectra were recorded with a Varian 4502 spectrometer equipped with standard temperature devices. The temperature was measured by means of a chromel–alumel thermocouple placed directly in the sample tube. The samples were degassed with nitrogen before photolysis with a high pressure mercury 100 W lamp using quartz optics. Coupling constants were verified by computer simulation using a Fortran IV program in which Lorentzian line shape was assumed.

Kinetics.—The decay of alkoxy aryl nitroxide radicals was measured at different temperatures by monitoring a single e.s.r. peak after interruption of the u.v. irradiation. First-order rate constants were obtained from least squares plots of the logarithm of peak height against time. The first-order rate constants did not change markedly on varying the concentration of the nitro-compounds by a factor of five.

Calculations.—INDO Calculations [22] were performed with a standard geometry, *i.e.* the total energy was not minimized with respect to all geometrical parameters.

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[18] K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1971, **93**, 902 and references therein.

[19] S. Brownstein, D. Linday, J. Dunogues, and K. U. Ingold, *J. Amer. Chem. Soc.*, in the press.

[20] L. R. Mahoney and S. A. Weiner, *J. Amer. Chem. Soc.*, 1974, **94**, 585, 1412.

[21] H. J. Den Hertog, jun., and J. Overhoff, *Rec. Trav. chim.*, 1930, **49**, 552; A. Kirpal and W. Böhm, *Ber.*, 1932, **65**, 680.

[22] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.